Online VOC measurements using Proton Transfer Reaction Ion Trap Mass Spectrometry on the Ronald Brown during TexAQS 2006

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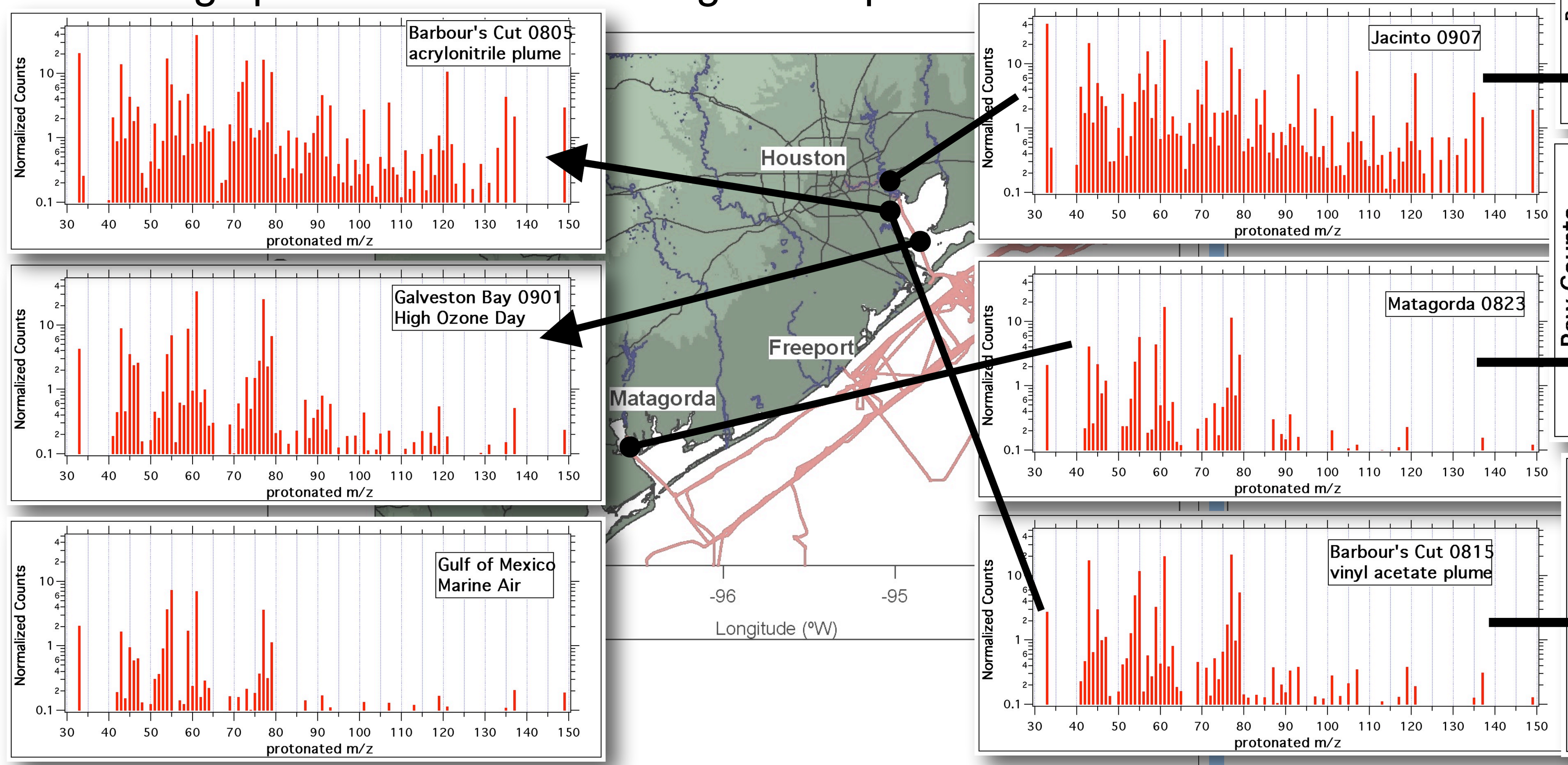
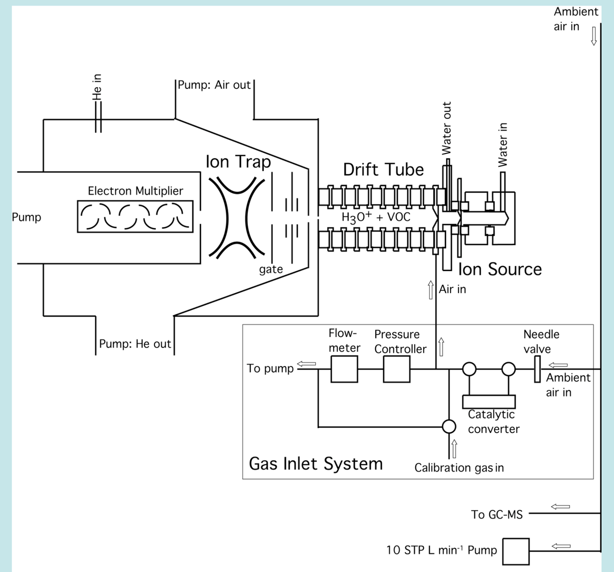
Online VOC measurements

During the cruise, a Proton Transfer Reaction Ion Trap Mass Spectrometer (PIT-MS) was used to generate a full mass spectrum (32-240 amu) for protonated VOCs every 10 seconds. The figure below shows some of the resulting spectra from areas along the ship track.



Proton Transfer Reaction Ion Trap Mass Spectrometry (PIT-MS)

- •Identical ion chemistry to PTR-MS instrument
- •Full Mass Spectrum in 10 sec
- •Final Data averaged to 1 min
- •Limit of detection at 1 min 0.5-1 ppbv for most species
- •97% Duty Cycle for all masses

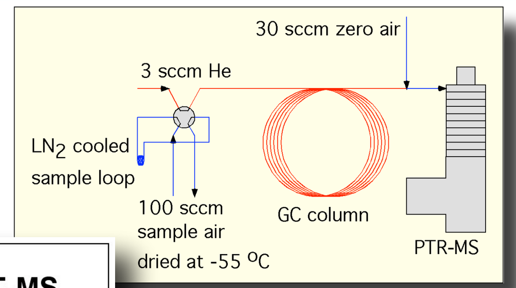


Compounds Reported

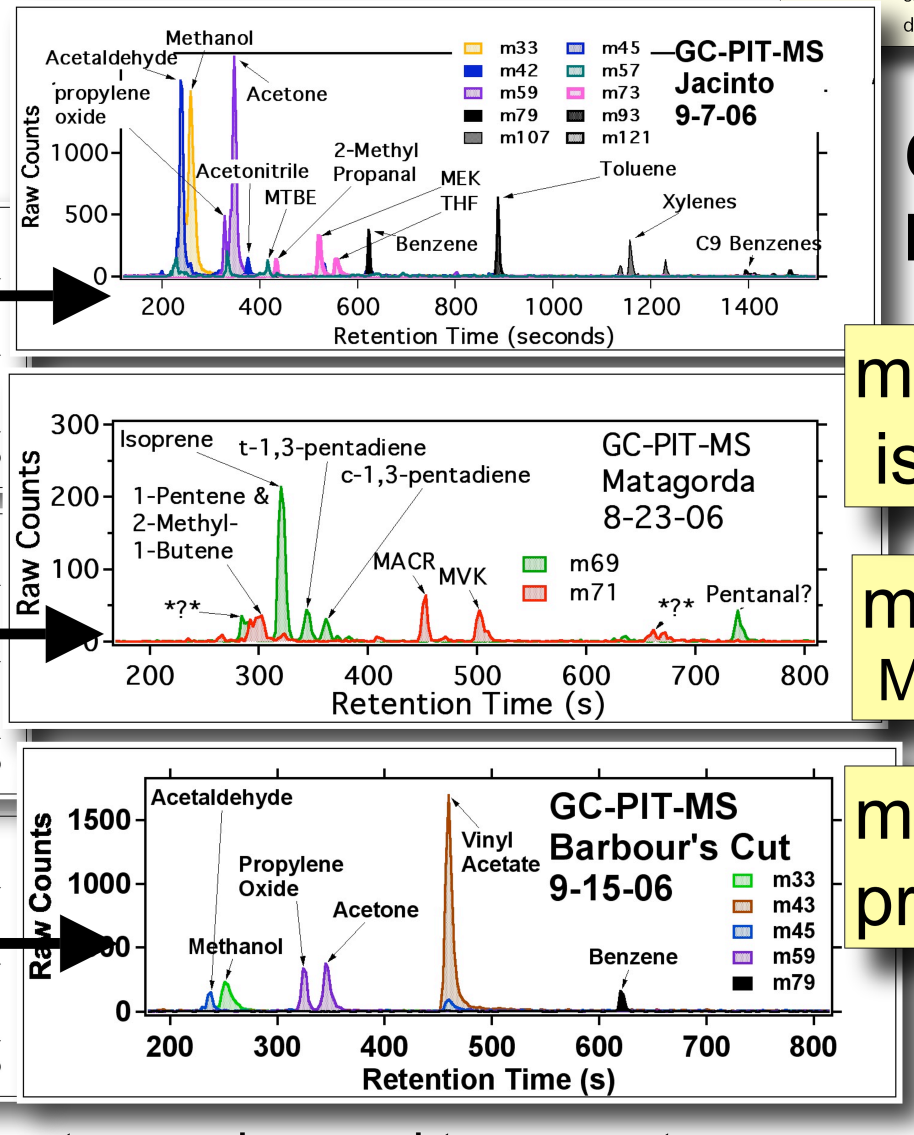
Oxygenates	Aromatics
methanol	benzene
acetone	toluene
acetic acid	xylenes
MEK	C9-C11 Benzenes
Alkenes/Biogenics/Others	
acetonitrile	monoterpenes
isoprene	
MVK+MACR	

GC-PIT-MS

During the cruise, a gas chromatograph was used periodically to concentrate and separate VOCs prior to analysis by PIT-MS.



Compound Identification

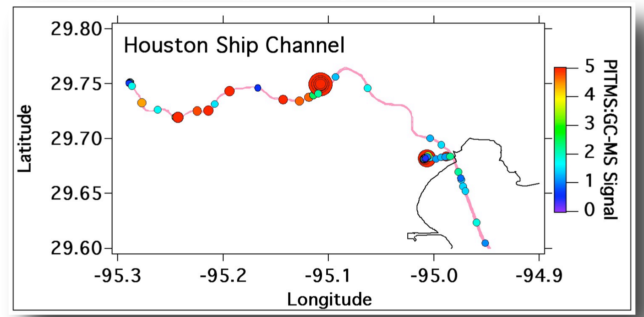


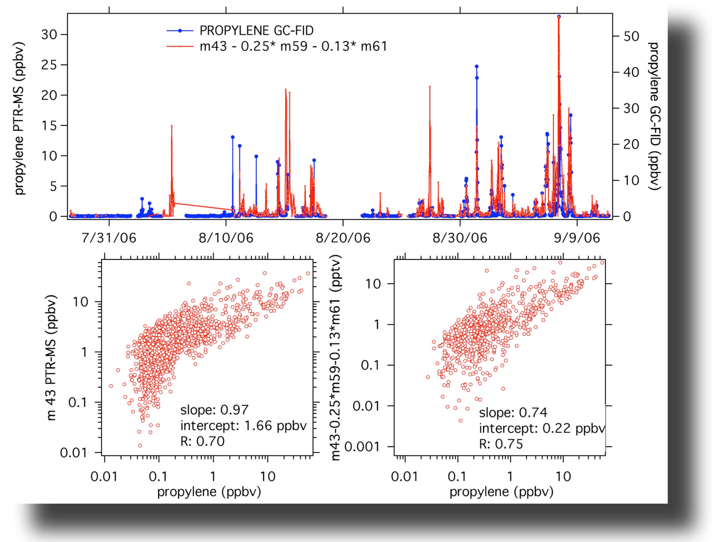
m69 not just isoprene

m71 not just MVK+MACR

m43 not just propylene

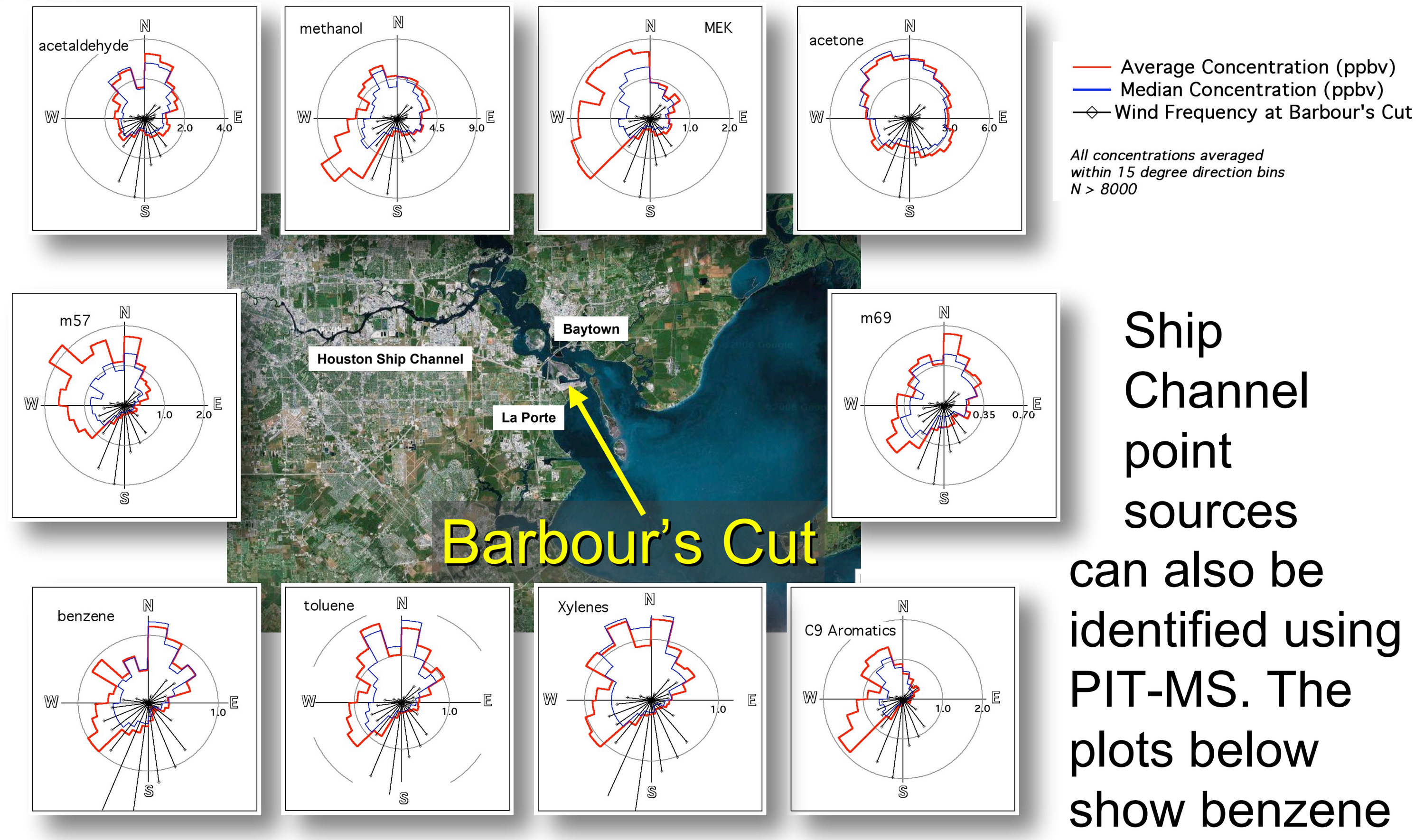
GC-PIT-MS spectra can be used to separate compounds with the same molecular mass. Caution must be used when interpreting PTR-MS signals from industrial areas like those found in the Houston/ Galveston area because of industrial emission of multiple compounds with the same molecular mass. For example, comparison of the signal at mass 69 with GC-MS isoprene measurements (above) reveal that industrial emissions can interfere with signals at this mass. The same is true at m71 which in other environments represents the sum of MVK + MACR. Similarly, fragments of multiple compounds occur at mass 43 confounding efforts to use this mass to monitor propylene in the Houston area (left).



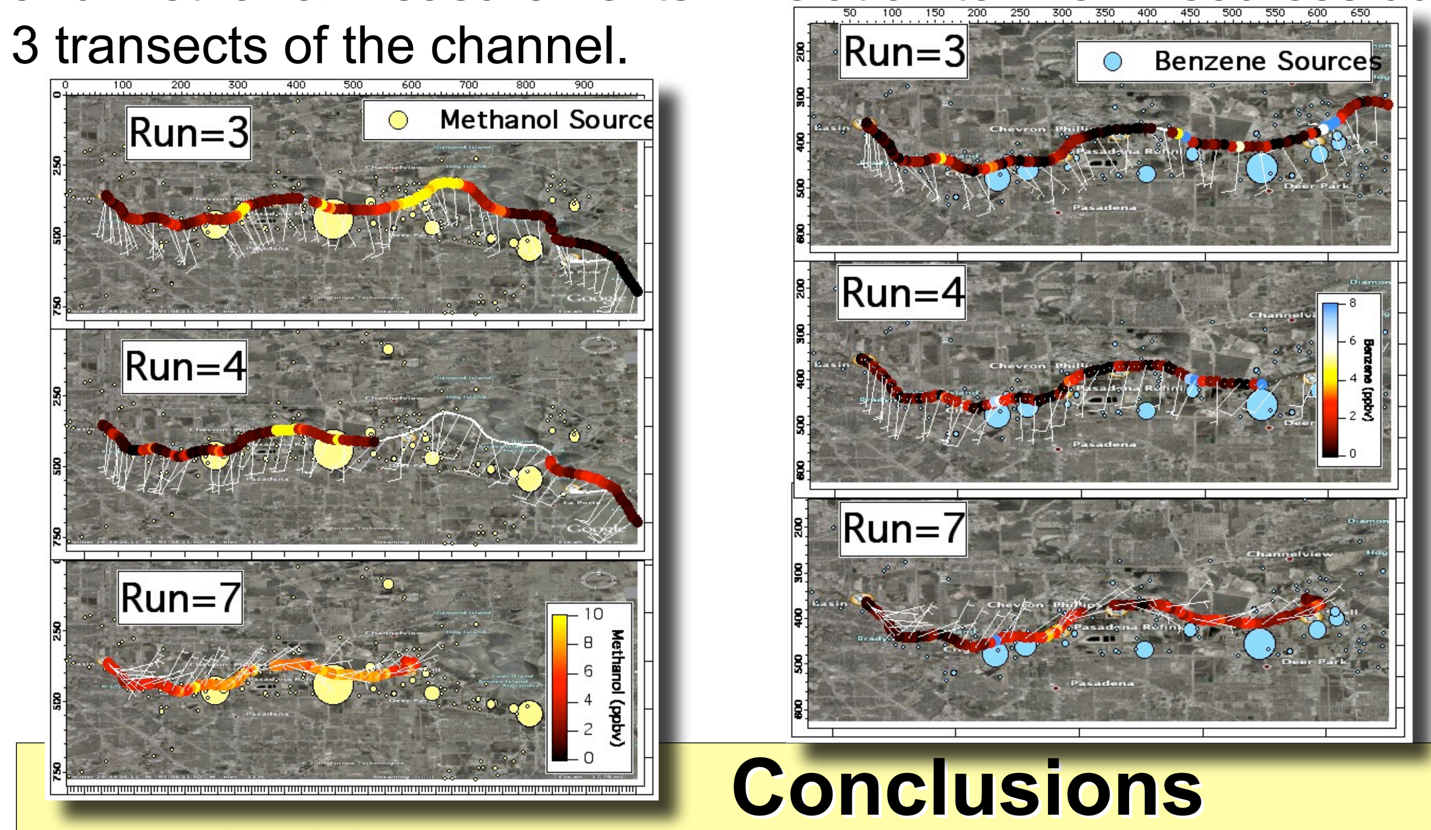


VOC Source Identification

The fast time response of the PIT-MS can be used to identify nearby VOC sources. On short time scales, wind direction points towards emission point sources. Wind rose plots from Barbour's Cut (below) show how VOC concentrations change with wind direction. RHB spent approximately 8 days sampling at this location.



Ship Channel point sources can also be identified using PIT-MS. The plots below show benzene and methanol measurements in relation to known sources during 3 transects of the channel.



Conclusions

- **•PIT-MS VOC data available at 10 sec time resolution for 15 standard masses and 100+ other masses**
- **•GC-PIT-MS shows industrial emissions interfere with standard PTR-MS interpretations at m43, m69, m71**
- **•High time resolution VOC and wind data can be used for local emission source identification**